

# Mercury and methylmercury content, fatty acids profile, and proximate composition of consumed fish in Cananéia, São Paulo, Brazil

Avaliação da concentração de mercúrio total e metilmercúrio e composição de ácidos graxos em pescado consumido em Cananéia, São Paulo, Brasil

RIALA6/1242

Michel Rodrigues da Silva Morales CURCHO<sup>1</sup>, Luciana Aparecida FARIAS<sup>1</sup>, Sueli Regina BAGGIO<sup>2</sup>, Barbara Cortopassi FONSECA<sup>1</sup>, Soraia Maria do NASCIMENTO<sup>1</sup>, Maritsa Carla de BORTOLI<sup>3</sup>, Elisabete de Santis BRAGA<sup>4</sup>, Déborah Inês Teixeira FÁVARO<sup>1\*</sup>

\*Endereço para correspondência: Laboratório de Análise por ativação com Nêutrons, Centro do Reator de Pesquisa Instituto de Pesquisas Energéticas e Nucleares (IPEN), São Paulo, SP, Brasil  
telefone: (011) 3133-9977, e-mail: defavaro@ipen.br

<sup>1</sup>Laboratório de Análise por ativação com Nêutrons Centro do Reator de Pesquisa, Instituto de Pesquisas Energéticas e Nucleares (IPEN), São Paulo, SP, Brasil

<sup>2</sup>Centro de Ciência e Qualidade de Alimentos, Instituto de Tecnologia de Alimentos (ITAL), , Campinas, SP, Brasil

<sup>3</sup>Laboratório de Alimentos e Nutrição Experimental, Faculdade de Ciências Farmacêuticas Universidade de São Paulo, São Paulo, SP, Brasil

<sup>4</sup>Laboratório de Nutrientes, Micronutrientes e Traços nos Oceanos (LABNUT), Instituto Oceanográfico, Universidade de São Paulo, São Paulo, SP, Brasil

Recebido: 05.05.2009 – Aceito para publicação: 08.12. 2009

## ABSTRACT

Fifty three individuals of four most commonly consumed fish species by the Cananéia city population, in São Paulo, Brazil, were analyzed to determine total mercury (Total Hg) and methylmercury (MeHg) levels, as well as, proximate composition and fatty acid profile. The muscle of three carnivorous species *Centropomus parallelus* (Fat snook), *Macrodon ancylodon* (King weakfish) and *Micropogonias furnieri* (Whitemouth croaker), and one planktivorous species *Mugil platanus* (Mullet) were analyzed. MeHg and Total Hg determinations were performed by Cold Vapour Atomic Absorption Spectrometry (CV AAS). Fatty acid profile was determined by gas chromatography (GC) whilst AOAC methods were used for proximate analysis. The total Hg results (interval) in wet weight basis were: Whitemouth croaker (114–442  $\mu\text{g kg}^{-1}$ ), Fat snook (15–178  $\mu\text{g kg}^{-1}$ ), King weakfish (12–100  $\mu\text{g kg}^{-1}$ ) and Mullet (<10–25  $\mu\text{g kg}^{-1}$ ), and none of the fish species exceeded the Brazilian legislation limits. MeHg values were below FAO/WHO (2007) recommendations. In nutritional terms, the results for proximate composition for all four fish species proved to be an excellent protein source with very low lipid content as was expected. Fatty acids of all fish species were adequate. Total polyunsaturated fatty acid contents varied from 21.9% (*Micropogonias furnieri*) to 26.4% (*Mugil platanus*). For the n-3 family, *Macrodon ancylodon* presented the highest value (20.9%) and *Micropogonias furnieri* the lowest one (15.8%). *Mugil platanus* (Mullet) species also showed good levels for all parameters analyzed and very low concentrations of contaminants, indicating it as a good nutritional choice in terms of risks and benefits.

**Key words.** mercury, methylmercury, proximate composition, fatty acids, fish, Cananéia

## RESUMO

Cinquenta e três amostras de músculo de pescados mais consumidos pela população de Cananéia, foram avaliados em relação aos teores de mercúrio total (HgT) e metilmercúrio (MeHg), composição centesimal e de ácidos graxos. Os músculos de três espécies carnívoras *Centropomus parallelus* (Robalo Peba), *Macrodon ancylodon* (Pescada) e *Micropogonias furnieri* (Corvina), e uma espécie planctívora, *Mugil platanus* (Tainha) foram analisadas. As determinações de Hg total e MeHg foram feitas por espectrometria de absorção atômica com geração de vapor frio (CV AAS). A composição de ácidos graxos foi determinada por cromatografia a gás (GC) e a composição centesimal, de acordo com as metodologias preconizadas pela AOAC. Os intervalos de concentração obtidos para Hg total (peso úmido) foram: Corvina (114–442  $\mu\text{g kg}^{-1}$ ), Robalo (15–178  $\mu\text{g kg}^{-1}$ ), Pescada (12–100  $\mu\text{g kg}^{-1}$ ) e Tainha (<10–25  $\mu\text{g kg}^{-1}$ ), não excedendo os limites da legislação brasileira. Os valores de MeHg se encontraram abaixo das recomendações da FAO/WHO(2007). Em termos nutricionais, os resultados de composição centesimal para todas as espécies analisadas provaram ser uma excelente fonte de proteína com conteúdo muito baixo de lipídeos. Os teores de ácidos graxos poliinsaturados totais variaram de 21,9% (Pescada) a 26,4% (Tainha). Para a família n-3, *Macrodon ancylodon* apresentou o maior valor (20,9%) e *Micropogonias furnieri*, o menor (15,8%). A espécie *Mugil platanus* apresentou níveis adequados para todos os parâmetros analisados e baixa concentração para os contaminantes, indicando-o como uma boa escolha nutricional em termos de riscos e benefícios.

**Palavras-chave.** mercúrio, metilmercúrio, composição centesimal, ácidos graxos, pescado, Cananéia.

## INTRODUCTION

Lipids in fish, as well as, fatty acid composition have been receiving a great deal of attention by researchers in the last years, due to their beneficial effects on human health. This has occurred at parallel to the development of equipment and methodological analysis techniques. The advances of these developments have permit the association of the structure of some fatty acids, especially n-3 and n-6 families, with the essentiality, biochemical metabolism and importance of these fatty acids in different fish species (saltwater and freshwater) and its role in human health<sup>1</sup>.

Fish constitute an important source of protein for many people throughout the world. As such, fish consumption has increased in importance among health-conscious people<sup>2</sup>. Fish represent also a healthy source of protein, providing omega-3 (n-3) the fatty acids that reduce cholesterol levels, and reduce the incidence of heart disease, stroke and pre-term deliveries<sup>3</sup>. At the same time, contaminant levels in fishes have considerable interest because of the potential effects on the fish themselves and the organisms that consume them, top-level receptors, including humans<sup>2</sup>. Thus, recently a number of researchers have started quantitative estimates of risks vs. benefits of fish intake on human health.

Since fish fauna serves as an important food source, it is essential to know the impact of water pollution on these organisms considering the action of the bioaccumulation and biomagnification processes. Any change in the natural conditions of aquatic medium causes several physiological adjustments in fish<sup>4</sup>. Given the fact that chemical constituents vary greatly from species to species, as well as, from individual to individual of the same species due to differences in seasons, locations, habitat, gender, age and feeding habits, it is important to know the composition and nutritional value of some Brazilian fish species consumed by coastal populations.

In this study, 53 individuals of the four most commonly consumed fish species by the Cananéia city population, São Paulo State, Brazil, were analyzed to determine contaminants, *i.e.*, total mercury (Total Hg) and methylmercury (MeHg), as well as, proximate composition and fatty acid profile. Cananéia population has a very peculiar characteristic in that it consumes large amounts of fish due to the fact that there are large number of individuals who make their living through fishing.

## MATERIAL AND METHODS

### Environmental aspects of the study area

The Cananéia-Iguape estuarine-lagoon complex is one of the world's most important marine life areas. In 1999 it received the UNESCO recognition as Natural Patrimony of Humanity. The Cananéia Island, located at the southern region represents a large portion of the system under natural conditions, *i.e.* less affected by anthropic influences.

The Cananéia-Iguape Estuary is composed of four water bodies and four islands. The population's main source of income is tourism and fishing. The region's population according to the 2006 Brazilian census is 14.195<sup>5</sup>. Due to the presence of mangroves on the banks of the estuary, high organic matter content and phytoplankton production are favored, consequently with a great abundance of fish and marine life<sup>6</sup>.

### Sampling and sample preparation

The fish samples were acquired directly from local fisheries in Cananéia during August of 2007. All samples acquired in local markets were assessed for quality indicators and external organoleptic characteristics (eyes, gills and scales). The species *Centropomus parallelus*, *Macrodon ancylodon*, *Micropogonias furnieri* and *Mugil Platanus* were analyzed. These species are the most consumed by Cananéia inhabitants. This information was taken from Farias et al<sup>7</sup>. Fish were conditioned in isothermic boxes in crushed ice and identified<sup>8</sup>. Once in the laboratory fish were evaluated according to total length, total weight and body weight. After this, individual muscle tissues were separated and dried at 50<sup>0</sup> C until constant weight. Dried samples were ground, homogenized and prepared for chemical analysis. These analyses were performed at the Neutron Activation Analysis Laboratory - IPEN.

For proximate composition and fatty acids profile a pool of each fish species analyzed was prepared. The pool was prepared from similar amounts of each individual sample of each species. After mixture of the individual samples they were again homogenized, resulting in a pool for each species: *Centropomus parallelus*, *Macrodon ancylodon*, *Micropogonias furnieri* and *Mugil Platanus*.

### Total mercury and methyl mercury determination

Mercury (Hg) and methyl mercury (MeHg) determination were performed using Cold Vapor Atomic

Absorption Spectrometry (CV AAS), using a FIMS from Perkin Elmer. For total Hg determination about 200 to 500 mg of fish samples were digested with a mixture of concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  in Teflon vials. The vials were closed and left overnight at room temperature. The following day, the vials were put into an aluminum block at  $90^\circ\text{C}$  and left there for 3 hours. The samples were allowed to cool at room temperature and the final volume was completed to 50 mL with Milli-Q water. For MeHg determination, the methodology was based on the leaching of the sample with 6M HCl, separation of organic from inorganic Hg through an ionic exchange resin (1 mL of ionic exchange resin - Dowex 1-X8. 200-400 mesh) used to separate non-ionic Me-HgCl from a  $\text{HgCl}_4^{2-}$  complex, retained on the column. After separation, samples were digested in a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  and mercury determination done by using CV AAS.

The analytical procedure used (wet digestion) was that of Horvat<sup>9</sup> with some modifications. This technique has many significant advantages in comparison with the conventional batches procedures, as lower consumption of sample solutions and reagents, simplicity for Hg determination, high sensitivity and relative freedom from interference. The peak area signals were measured and the Hg content of the samples was calculated against the Hg standard curves. The  $\text{Hg}^{2+}$  is reduced on line by  $\text{SnCl}_2$  1.1% (m/v) in HCl 3% (v/v) at a flow of 5 – 6 mL  $\text{min}^{-1}$ . Argon was used as a carrier gas at a constant flow of 100 mL  $\text{min}^{-1}$ . All analytical methods were developed and validated for precision and accuracy by means of reference materials analyses with certified values for the elements determined: Dogfish muscle (DORM-1, NRCC) and Dogfish liver (DOLT-1, NRCC).

### Proximate Composition

Determination of humidity, ash and proteins were performed according to the AOAC methodologies<sup>10</sup>. Since there were not enough samples for all analyzes and carbohydrates are not a regular component of fresh fish, lipid content was calculated from the difference of the total amount of humidity, ash and proteins.

Lipid profile was converted to relative values of g/100g of fish. The energetic value was calculated applying the Atwater factors 4 – 9 – 4 – 7 kcal/g of protein, lipids, carbohydrates and alcohols, respectively. These analyzes were undertaken at the Food and Experimental Nutrition Laboratory of the Pharmaceutical Science Institute (USP-SP).

### Fatty acid determination

#### *Lipid extraction according to Bligh & Dyer methodology<sup>11</sup>*

The wet tissue was homogenized with a mixture of chloroform and methanol in such proportions that a miscible system is formed with the water in the tissue. Dilution with chloroform and water separates the homogenate into two layers, the chloroform layer containing all the lipids and the methanolic layer containing all the non-lipids. A purified lipid extract is obtained merely by isolating the chloroform layer<sup>11</sup>. This procedure was undertaken at LAN, the lipid extracts were frozen and then sent to Institute of Food Technology (ITAL) for fatty acid determination.

#### *Fatty acid determination*

The analyses were performed at the Center for Food Science and Quality from ITAL, Campinas. For fatty acid determination, one aliquot of lipid extract containing approximately 400 mg for each pool of fish species analyzed was taken and dried in a rotatory evaporator. The transmethylation was done according to Hartman & Lago methodology<sup>12</sup>, using ammonium chloride solution and sulfuric acid in methanol as an esterificand agent. The gas chromatography was performed using a gas chromatography, (Varian, model 3900, Palo Alto, California, USA) equipped with an auto sampler; injector split, ratio 1/75; fused silica capillary column (100 m x 0.25 mm i.d., 0.20  $\mu\text{m}$  film thickness) (CP-SIL 88, Chrompack, Middelburg, The Netherlands) and flame ionization detector. The initial column temperature was  $120^\circ\text{C}$  for 5 minutes and then programmed to increase at 5-C/min to  $235^\circ\text{C}$ ; the injector temperature was set at  $270^\circ\text{C}$ ; the detector temperature at  $300^\circ\text{C}$ ; injection volume was 1  $\mu\text{L}$ . The carrier gas was hydrogen at a flow rate of 1 mL/min and nitrogen was used as the make-up gas at 30 mL/min. The fatty acids were identified by comparison of the retention times of the sample with those of the standards and by spiking. To verify the identity and accuracy of the method a total of 37 saturated, monounsaturated and polyunsaturated fatty acid standards (37 FAME Mix 47885-U, Sulpeco<sup>TM</sup>, Bellefonte, PA, USA) were used. Quantification was done as area percentages and the results were expressed in % of area.

## RESULTS AND DISCUSSION

The methodology validation for total Hg and MeHg for CV AAS were carried out by reference materials

analyses. The results are presented in Table 1. For total Hg the relative standard deviation (RSD) varied from 1.7 to 11.7% and relative error (RE), from 0.9 to 2.6 %. For MeHg determination relative standard deviation ranged from 3.1 to 8.0% and relative error, from 1.4 to 12.0%, showing the precision and accuracy of both analytical methodologies, respectively.

Table 2 presents mean and concentration intervals for total Hg ( $\mu\text{g kg}^{-1}$ ) and Me Hg contents (%) by CV AAS, in dry and wet weight, total weight and total length for the fish species analyzed. The total Hg averages and ranges (wet weight basis) for the species analyzed were:  $236 \pm 111 \mu\text{g kg}^{-1}$  (114 - 442) for *Micropogonias furnieri* (Whitemouth croaker);  $42 \pm 24 \mu\text{g kg}^{-1}$  (12 - 100) for *Macrodon ancylodon* (King weakfish);  $48 \pm 43 \mu\text{g kg}^{-1}$  (15 - 178) *Centropomus parallelus* (Fat snook) and  $8.3 \pm 5.6 \mu\text{g kg}^{-1}$  (<10 - 25) for *Mugil platanus* (Mullet), respectively.

The total Hg averages and ranges (dry weight basis) were:  $1071 \pm 504 \mu\text{g kg}^{-1}$  (516 - 2008) for *Micropogonias furnieri*;  $191 \pm 109 \mu\text{g kg}^{-1}$  (56 - 456) for *Macrodon ancylodon*;  $193 \pm 173 \mu\text{g kg}^{-1}$  (61 - 712) for *Centropomus parallelus* and  $33 \pm 22 \mu\text{g kg}^{-1}$  (<10 - 98) for *Mugil platanus*, respectively. MeHg averages and ranges (dry weight) for these species were:  $652 \mu\text{g kg}^{-1}$  (227 - 1487),  $171 \mu\text{g kg}^{-1}$  (37 - 452);  $88 \mu\text{g kg}^{-1}$  (22 - 399) and  $< 10 \mu\text{g kg}^{-1}$ , respectively. In relation to total Hg values, MeHg concentration values corresponded to 34 to 85% in *Micropogonias furnieri*, 37 to 99% in *Macrodon ancylodon* and 18 to 61% in *Centropomus parallelus*. The concentration values for *Mugil platanus* species were too low for MeHg determination.

Concerning populational risk to toxic element exposure, Hg and MeHg, Hg did not exceed the Brazilian legislation limits<sup>13</sup> for predatory ( $1000 \mu\text{g Hg kg}^{-1}$ ) and non predatory species ( $500 \mu\text{g kg}^{-1}$ ), in wet weight. For MeHg there is no limit in the Brazilian legislation, but the values were bellow FAO/WHO recommendations of  $1000 \mu\text{g Hg kg}^{-1}$  for MeHg levels in predatory species and  $500 \mu\text{g kg}^{-1}$  in non-predatory ones<sup>14</sup>.

Table 3 shows the results obtained for the fatty acid profile for the pool of the fish species analyzed. Total saturated fatty acids ranged from 28% in *Macrodon ancylodon* to 41.8% in *Mugil platanus*. Total polyunsaturated fatty acid contents varied from 21.9% in *Micropogonias furnieri* to 26.4% in *Mugil platanus*. These species presented similar proportions of polyunsaturated fatty acids of the n-3 family (average 17.8%) and of the n-6 family (average 7.0%).

Regarding the n-6 family *Mugil platanus* species showed the highest values (8.9%) and *Macrodon ancylodon*, the lowest ones (4.4%). On the other hand, for the n-3 family, *Macrodon ancylodon* presented the highest value (20.9%) and *Micropogonias furnieri* the lowest one (15.8%).

Lipid composition in fish tissues can be affect by diet and environmental factors such as salinity, temperature, seasons and geographical location. Although several marine fish species are rich in polyunsaturated fatty acids n-3 family, their levels can vary according to different species. Eicosapentaenoic (EPA) (C20:5 n-3) and docosahexaenoic (DHA) (C22:6 n-3) fatty acids of the

**Table 1.** Results for total Hg and Me Hg in the certified reference materials by CV AAS (n = 5)

Certified Reference Materials	Hg <sub>total</sub> (mean ± s.d.)	Certified Value	RSD (%)	RE (%)	MeHg (mean ± s.d.)	Certified Value	RSD (%)	RE (%)
DOLT-3 (Dogfish Liver) (mg kg <sup>-1</sup> )	3.4 ± 0.4	3.37 ± 0.14	11.7	0.9	1.40 ± 0.1	1.59 ± 0.12	8.0	12.0
DORM-1 NRCC (Dogfish Muscle) (mg kg <sup>-1</sup> )	777 ± 13	798 ± 74	1.7	2.6	740 ± 23	731 ± 60	3.1	1.4

n – number of determinations

**Table 2.** Mean and concentration interval for total Hg ( $\mu\text{g kg}^{-1}$ ) and Me Hg contents (%) by CV AAS (dry and wet weight), total weight and total length for the fish species analyzed

Fish species	Feed Habits	Total weight (g)	Total length (mm)	Total Hg Muscle (wet weight)	Total Hg Muscle (dry weight)	MeHg (interval) (%)
<i>Micropogonias furnieri</i> (Whitemouth croaker) (11)	Detritivorus	1199 ± 231 (832-1399)	461 ± 25 (414 – 507)	236 ± 111 (114 – 442)	1071 ± 504 (516 – 2008)	(34 – 85)
<i>Macrodon ancylodon</i> (King weakfish) (16)	Carnivorous	321 ± 99 (239 – 613)	283 ± 113 (281 – 340)	42 ± 24 (12 – 100)	191 ± 109 (56 – 456)	(37 – 99)
<i>Centropomus parallelus</i> (Fat snook) (12)	Carnivorous	474 ± 76 (312 – 563)	388 ± 32 (318 – 424)	48 ± 43 (15 – 178)	193 ± 173 (61 – 712)	(18 – 61)
<i>Mugil platanus</i> (Mullet) (14)	Planktivorus	1469 ± 347 (807 – 1936)	544 ± 51 (432 – 600)	8.3 ± 5.6 (<10 – 25)	32 ± 22 (<10 – 98)	-

(n) – number of samples analyzed

n-3 family are abundant in various marine fish species, specifically those that feed on polyunsaturated fatty acid n-3 family rich-plankton.

Omega-3 and 6 fatty acids are essential for human beings, but they are not synthesized by the body. Their deficiency can provoke adverse health effects. These fatty acids are constituents of cellular structure and are needed for membrane formation<sup>15</sup>. Omega-6 deficiency can provoke dermatological symptoms, while n-3 deficiency is related to neurological and visual disturbances<sup>16</sup>.

In the four fish species analyzed, the predominancy of unsaturated fatty acids in relation to total lipids (50.4 to 67.2%) could be observed. The higher concentration of monounsaturated fatty acids ranged from 24.7 % (Mullet) to 41.9% (King weakfish) (Table 3). The fatty acid composition revealed that the most abundant were palmitic acid (C16:0) and oleic acid (C18:1 n9) ; palmitoleic acid (C16:1 n7) and stearic acid (C18:0) in lower proportions in the four fish species analyzed with levels ranging from 12.1 to 27.7%, from 11.9 to 28.6%, 4.9 to 12.0% and from 4.9 to 13.9%, respectively of the total fatty acids. Among the fish species analyzed *Centropomus parallelus* presented the highest proportion of palmitic acid (27.7%) and *Macrodon ancylodon*, the

highest proportion of oleic (28.6%), palmitoleic (12.0%) and stearic acids (13.9%). The (EPA + DHA) fatty acid levels were higher for *Macrodon ancylodon* (18.5%) and lower for *Micropogonias furnieri* (11.9%).

As is already known, fish chemical composition can vary in function due to several endogenous and exogenous factors such as: genetics, size, gender, reproductive age, feeding habits, environmental factors, temperature and seasons<sup>17, 18</sup>.

According to published literature, consumption of n-6/n-3 ratio ranging from 5:1 to 10:1 is recommended for adults for the prevention of cardiovascular risks<sup>19</sup>. Even though in the present study n-6/n-3 ratio ranged from 0.21 (*Macrodon ancylodon*) to 0.51 (*Mugil platanus*), it must not be forgotten that fish is only a small part of a whole diet. Therefore it could be an important contribution in reaching the recommended ratio.

Table 4 presents the results obtained for proximate composition in the fish pool samples and literature values from TACO2<sup>20</sup>, USDA<sup>21</sup> and Menezes<sup>22</sup> for comparison for all fish species analyzed. For the *Micropogonias furnieri* species, in general, the obtained values were similar to the literature<sup>20</sup>. However, the results for fatty acid n-3 family were higher and total lipids lower.

**Table 3.** Fish species (muscle pool) fatty acid composition, expressed in area (%) of the relative area concerning the total lipids

<b>Fatty acids</b>	<b><i>Micropogonias furnieri</i> (Whitemouth croaker)</b>	<b><i>Macrodon ancylodon</i> (King weakfish)</b>	<b><i>Centropomus parallelus</i> (Fat snook)</b>	<b><i>Mugil platanus</i> (Mullet)</b>
C 13:0	Nd	Nd	nd	0.1
C 14:0	2.7	0.7	1.5	4.4
C 15:0	0.7	0.1	1.1	6.8
C 15:1	Nd	Nd	nd	0.3
C 16:0	26.3	12.1	27.7	22.5
C 16:1n7	10.7	12.0	4.9	8.1
C 17:0	0.8	0.2	1.2	1.7
C 17:1	0.7	0.1	1.4	3.7
C 18:0	7.0	13.9	8.2	4.9
C 18:1n9t	0.4	0.4	0.4	0.3
C 18:1n 9	17.3	28.6	17.6	11.9
C 18:2n6t	0.1	nd	0.6	0.2
C 18:2n6	1.3	0.8	2.1	3.3
C 20:0	0.4	0.6	0.3	0.2
C 18:3n3t	0.1	nd	0.1	0.5
C 20:1n11	1.4	0.8	0.8	0.4
C 18:3n3	0.7	0.4	0.6	1.3
C 21:0	0.1	nd	nd	nd
C 20:2n6	0.8	0.5	0.3	1.4
C 22:0	0.3	0.2	0.5	1.2
C 20:3n6	0.2	0.1	0.2	0.2
C 20:3n3	0.2	nd	0.1	0.1
C 22:1	0.2	0.1	0.1	0.2
C 20:4n6	3.4	2.7	5.7	3.4
C 22:2n6	0.4	0.3	0.1	0.6
C 24:0	Nd	0.2	0.3	nd
C 20:5n3	4.6	3.9	1.9	5.9
C 24:1	0.3	0.3	0.2	0.1
C 22:5n3	3.0	2.0	2.6	4.1
C 22:6n3	7.3	14.6	11.8	6.1
Σ Saturated	38.3	28.0	40.8	41.8
Σ Monounsaturated (MUFA)	30.6	41.9	25.0	24.7
Σ Polyunsaturated (PUFA)	21.9	25.3	25.4	26.4
Σ omega 6	6.1	4.4	8.4	8.9
Σ omega 3	15.8	20.9	17.0	17.5
Trans	0.6	0.4	1.1	1.0
NI	8.6	4.4	7.7	6.1
Σ (MUFA+PUFA)	52.5	67.2	50.4	51.1
n-6/ n-3	0.39	0.21	0.49	0.51
Σ (EPA+DHA)	11.9	18.5	13.7	12.0

nd = not detected (detection limit 0.1%); N.I. = not identified

**Table 4.** Analyzed fish samples (pool) proximate composition and TACO2<sup>20</sup>, USDA<sup>21</sup> and Menezes<sup>22</sup> data for comparison

Fish species	<i>Micropogonias furnieri</i> (Whitemouth croaker)	<i>Macrodon ancylodon</i> (King weakfish)	<i>Centropomus parallelus</i> (Fat snook)	<i>Mugil platanus</i> (Mullet)	TACO2 <sup>20</sup> (Whitemouth croaker)	TACO2 <sup>20</sup> (King weakfish)	USDA <sup>21</sup> (Mullet)	Menezes <sup>22</sup> <i>Centropomus undecimalis</i> (Common snook)	Menezes <sup>22</sup> <i>Mugil cephalus</i> (Tainha)
Humidity	77.9 ± 1.7	77.8 ± 4.9	76 ± 5.7	75.1 ± 3.0	79.4	79.5	77.0	79.6 ± 1.1	78.4 ± 1.6
Ash	1.06	1.07	1.17	1.26	1.1	0.9	1.2	1.09 ± 0.15	1.06 ± 0.13
Proteins	19.6	18.8	20.1	20.9	18.6	16.7	19.35	18.3 ± 1.2	20.8 ± 1.6
Lipids <sup>1</sup>	1.46	2.35	2.75	2.71	1.6	4	3.79	2.5 ± 0	2.5 ± 0
Lipids profile <sup>2</sup>									
Saturated	0.56	0.66	1.12	1.13	0.7	0.9	1.116		
Monounsaturated	0.45	0.98	0.69	0.67	0.5	2.3	1.078		
Polyunsaturated	0.32	0.59	0.7	0.72	0.1	0.3	0.715		
Ômega 6	0.09	0.10	0.23	0.24	0.1	0.03	0.088		
Ômega 3	0.23	0.49	0.47	0.47	0.02	0.02	0.025		
Trans	0.008	0.009	0.03	0.03					
Not identified	0.12	0.10	0.21	0.16					
Energy <sup>3</sup>	91.4	96.3	105.1	108.1	94	107	117		

<sup>1</sup> Fats calculated over humidity, ashes and proteins values

<sup>2</sup> Lipid profile calculated and expressed over total lipid content

<sup>3</sup> Energy in kcal

For *Macrodon ancylodon* species, the results for protein were higher than the literature, as well as, for polyunsaturated fatty acids and n-3 and n-6 fractions.

The results for *Mugil platanus* species were compared to the USDA National Nutrient Database for Standard Reference (Release 18)<sup>21</sup>. The lipid content was lower than the literature and higher for polyunsaturated fatty acids of the n-3 and n-6 families. Comparing the values with literature for *Mugil platanus* from Menezes<sup>22</sup> similar values were observed.

The results obtained for *Centropomus parallelus* in the present study were compared to the results obtained for *Centropomus undecimalis* data presented from Menezes<sup>22</sup> and values were similar as well.

The fishes analyzed presented different values in their chemical composition (Table 4). The humidity values ranged from 75.1% in *Mugil platanus* to 77.9% in *Micropogonias furnieri*, while ash content observed was lower in *Micropogonias furnieri* and higher in *Mugil platanus* species. The average protein content was  $19.9 \pm 0.9\%$  with a very narrow protein content interval (from 18.8 to 20.9%).

*Micropogonias furnieri*, *Macrodon ancylodon* and *Mugil platanus*, in general, presented protein values higher than those found in the literature (Table 4).

For polyunsaturated fatty acids *Mugil platanus* presented similar values to those found in the literature, and *Micropogonias furnieri* and *Macrodon ancylodon* presented higher values. Regarding n-3 and n-6 contents for the four species, the results were, in general, higher than those values published in the literature (Table 4).

## CONCLUSION

Concerning populational risk to toxic element exposure, Hg and MeHg, Hg did not exceed the Brazilian legislation limits<sup>13</sup> for predatory ( $1000 \mu\text{g Hg kg}^{-1}$ ) and non-predatory fish species ( $500 \mu\text{g kg}^{-1}$ ), in wet weight basis. For MeHg the value set by FAO/WHO<sup>14</sup>, of  $1000 \mu\text{g Hg kg}^{-1}$  for predatory fish species and  $500 \mu\text{g kg}^{-1}$  in non-predatory ones, were not found in the studied samples. Even if mercury or methylmercury were found in the fish, levels would be considered safe for consumption, although the amount of fish that the population indeed consumes on a daily or weekly basis must be assessed.

In this study the whole diet of Cananéia's population was not assessed, but as fish play an important role for the population, from the nutritional point of view

the results for proximate composition for all four species showed that these fishes can be an excellent protein source with very low lipid content, as was expected. Regarding the fatty acid profile, all fish species analyzed were also adequate.

*Micropogonias furnieri* (Whitemouth croaker) presented higher total Hg content because it is a predatory species. *Mugil platanus* (Mullet), however, showed good levels for all parameters analyzed and very low concentrations of total Hg and MeHg, indicating that this may be a good nutritional choice in terms of risks and benefits. Unfortunately this species has seasonal availability and is relatively expensive and *Macrodon ancylodon* (King weakfish) is much more consumed.

## REFERENCES

1. Souza SMG, Anido RJ, Tognon FC. Fatty acids Omega-3 and Omega-6 in fish nutrition – sources and relations. *Revista Ciências Agroveterinárias*. 2007; 6(1): 63-71.
2. Burger J, Gochfeld M. Heavy metals in commercial fish in New Jersey. *Environmental Research*. 2005; 99: 403–12.
3. Anderson PD, Wiener JB. Eating fish. In: Graham JD, Wiener JB, editors. *Risk versus Risk: Tradeoffs in Protecting Health and the Environment*. Harvard, University Press, Cambridge, MA.,1995, p. 104–23.
4. Black EC. Blood levels of hemoglobin and lactic acid in some freshwater fishes following exercise. *J. Fish. Res. Bd., Canada*.1955; 12 (6): 917 - 9.
5. Instituto Brasileiro de Geografia e Estatística [IBGE], 2006. *IBGE Cidades@*. Site: <http://www.ibge.gov.br>. (Acesso em 11mar 2008).
6. Garcia TR. Impactos da implantação de uma cooperativa de produção de ostras junto a comunidades extrativistas caieiras do litoral sul/SP: um estudo de caso [Tese de Doutorado]. São Paulo, Universidade de São Paulo, Faculdade de Zootecnia e Engenharia de Alimentos, 2005.
7. Farias LA, Santos NR, Fávoro DIT, Braga ES. Mercúrio total em cabelo de crianças de uma população costeira, Cananéia, São Paulo, Brasil. *Cad. Saúde Pública*, Rio de Janeiro. 2008; 24(10): 2249-56.
8. Figueiredo JL, Menezes NA. Manual de peixes marinhos do Sudeste do Brasil III. Teleostei (2). São Paulo: Museu de Zoologia, Universidade de São Paulo, 1980, 90p.
9. Horvat, M. Mercury analysis and speciation in environmental samples. In W. Baeyens et al (eds), *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances* (NATO ASI Series, Partnership Sub-Series: 2), The Netherlands, Kluwer Academic Publishers, 1996, p.1-31.
10. Association of official analyst chemists. *Official methods of analysis* (AOAC). 16ª ed., 3ª rev. Gaithersburg: Published by AOAC International, 1997. v.2, cap. 32, p.1-43.
11. Bligh EG, Dyer WJ. A rapid method of total lipid extraction and purification. *Can. J. Biochem. Phys.*1959; 37(8): 911-7.
12. Hartman L, Lago RCA. Rapid preparation of fatty acid methyl esters from lipids. *Lab. Pract.* 1973; 22: 475-7.



13. Brasil. Ministério da Saúde. Secretaria de Vigilância Sanitária. Portaria nº 695 1998. . Diário Oficial [da] República Federativa do Brasil, Brasília, DF, p.5-6, 30 mar.1998. Seção 1.
14. FAO-WHO Additives series: 58. Safety evaluation of certain food additives and contaminants. Sixty-seventh meeting of the joint FAO/WHO Expert Committee on Food Additives (JECFA), 2007, 337p.
15. Santos KMO, Aquino RC. Grupo dos óleos e gorduras, In: Philippi, S. T. (Org), Barueri: Manole editora, 2008. p. 241-92.
16. Rogero MM, Gomes MR, Tirapegui J. Lipídeos In: de Angelis, R. C.; Tirapegui, J. (Org) Fisiologia da Nutrição Humana Aplicada: Aspectos Básicos, Aplicados e Funcionais. São Paulo, Atheneu editora, 2007, p. 49-68.
17. Luzia LA. et al. The influence of season on the lipid profiles of five commercially important species of Brazilian fish. *Food Chemistry*, Champaign. 2003, 83(1): 93-7.
18. Moreira AB. et al. Fatty acids profile and cholesterol contents of three Brazilian *Brycon* freshwater fishes. *Journal of Food Composition and Analysis*, London. 2001;14(6): 565-74.
19. National Academic Press. Dietary reference intakes for energy, carbohydrate, fiber, fat, fatty acids, cholesterol, protein, and amino acids (macronutrients). 1357p., 2005. Available from : <http://www.nap.edu/catalog/10490.html>. Accessed in January, 2009.
20. Tabela Brasileira de Composição de Alimentos (TACO 2) versão 2, 2ª edição - Núcleo de Estudos e Pesquisas em Alimentação – NEPA, Universidade Estadual de Campinas – UNICAMP, Campinas, 2006.
21. USDA Nutrient Database for Standard Reference, Release 18 (SR18), <http://www.ars.usda.gov/research/publications> accessed in February, 2009.
22. Menezes MES, Lira GM, Omena CMB, Freitas JD, Sant’Ana AEG. Proximate composition, cholesterol and fatty acid of the fished species of estuarino Tainha (*Mugil cephalus*) and Camurim (*Centropomus undecimalis*) from Mundaú Lagoon, Al/Brazil. *Rev Inst Adolfo Lutz*. 2008; 67(2): 89-95.